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Plasma-Assisted Processing of Gaseous Media

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The present invention relates to the plasma-assisted processing of gaseous media and in particular to the

5 reduction of the emissions of one or more of nitrogenous oxides, particulate including carbonaceous particulate, hydrocarbons including polyaromatic hydrocarbons, carbon monoxide and other regulated or unregulated combustion products from the exhausts of internal combustion

10 engines.

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One of the major problems associated with the development and use of internal combustion engines is the noxious exhaust emissions from such engines. Two of the

15 most deleterious materials, particularly in the case of diesel engines, are particulate matter (primarily carbon) and oxides of Nitrogen ( $\text{NO}_x$ ). Increasingly severe emission control regulations are forcing internal combustion engine and vehicle manufacturers to find more

20 efficient ways of removing these materials in particular from internal combustion engine exhaust emissions. Unfortunately, in practice, it is found that combustion modification techniques which improve the situation in relation to one of the above components of internal

25 combustion engine exhaust emissions tend to worsen the situation in relation to the other. A variety of systems for trapping particulate emissions from internal combustion engine exhausts have been investigated, particularly in relation to making such particulate

30 emission traps capable of being regenerated when they have become saturated with particulate material.

Examples of such diesel exhaust particulate filters are to be found in European patent application EP 0 010

384; US patents 4,505,107; 4,485,622; 4,427,418; and  
4,276,066; EP 0 244 061; EP 0 112 634 and EP 0 132 166.

In all the above cases, the particulate matter is  
5 removed from diesel exhaust gases by a simple physical  
trapping of particulate matter in the interstices of a  
porous, usually ceramic, filter body, which is then  
regenerated by heating the filter body to a temperature  
10 burnt off. In most cases the filter body is monolithic,  
although EP 0 010 384 does mention the use of ceramic  
beads, wire meshes or metal screens as well. US patent  
4,427,418 discloses the use of ceramic coated wire or  
ceramic fibres.

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In a broader context, the precipitation of charged,  
particulate matter by electrostatic forces also is known.  
However, in this case, precipitation normally takes place  
upon large planar electrodes of metal screens.

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GB patent 2,274,412 discloses a method and apparatus  
for removing particulate and other pollutants from  
internal combustion engine exhaust gases, in which the  
exhaust gases are passed through a bed of charged pellets  
25 of material, preferably ferroelectric, having high  
dielectric constant. In addition to removing  
particulates by oxidation, especially electric discharge  
assisted oxidation, there is disclosed the reduction of  
NO<sub>x</sub> gases to nitrogen, by the use of pellets adapted to  
30 catalyse the NO<sub>x</sub> reduction.

Also, US patents 3 983 021, 5 147 516 and 5 284 556  
disclose the catalytic reduction of nitrogen oxides.  
However, US 3 983 021 is solely concerned with the  
35 reduction of NO to N in a silent glow discharge, the

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temperature of which is kept below a value at which the oxidation of N or NO to higher oxides of nitrogen does not occur. There is no mention of any simultaneous removal of hydrocarbons.

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US patent 5 284 556 discloses the removal of hydrocarbons from internal combustion engine exhaust emissions. The process involved is one of dissociation in an electrical discharge of the so-called 'silent' type, that is to say, a discharge which occurs between two electrodes at least one of which is insulated. The device described is an open discharge chamber. Mention is made of the possible deposition of a NO<sub>x</sub>-reducing catalyst on one of the electrodes.

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A conventional dielectric barrier plasma assisted gas reactor such as that disclosed in specification US 5,284,556, consists of a plasma volume situated between two electrodes at least one of which has a dielectric barrier in the form of a thick layer of an insulating medium on its inner surface. JP-A-4027414 also discloses a dielectric barrier type of reactor in which electrodes, arranged parallel to the direction of gas flow, are positioned on opposite sides of a dielectric material through which bored holes provide gas passages.

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In order to generate a plasma in such a device, the potential within the space between the electrodes must reach a critical value before the plasma will ignite.

The potential which appears across the main plasma volume is dependent upon the ratio of the capacitance of the dielectric layer and that of the plasma volume because these two entities create a capacitive potential divider. The potential across the plasma volume is inversely proportioned to its capacitance, that is to say, the

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higher the capacitance of the plasma volume, the lower is the potential difference across it. This effect can cause a serious problem if the plasma volume is filled with a gas permeable material which has a high dielectric constant, such as pellets of barium titanate, because the potential difference across such a reactor bed may never reach the critical value for the plasma to ignite unless the supply voltage is very high, of the order of tens of kilovolts which may exceed the safe working voltage of the dielectric barrier, or other high voltage components of the power supply.

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It is an object of the present invention to provide an improved reactor for the plasma-assisted processing of a gaseous medium.

According to the invention in one aspect there is provided a reactor for the plasma assisted processing of a gaseous medium including a pair of electrodes having facing surfaces, the separation of the facing surfaces being substantially uniform and defining a space therebetween, and a body of dielectric material positioned to provide a dielectric barrier between the electrodes (1,2;21,22) and configured to divide the said space between the electrodes (1,2;21,22) into a plurality of gas passages (6;24), which together provide the plasma volume of the reactor and along the lengths of which gas flows in use of the reactor, the gas passages (6;24) being aligned so that their lengths extend between and in a direction parallel with the facing surfaces of the electrodes (1,2;21,22), the gas passages being spaced apart from one another in a direction transverse to the said facing surfaces, characterised in that the gas passages (6;24) are shaped so as to have a pair of opposed sides the contour of which matches the contour of the said facing surfaces of the electrodes (1,2;21,22),

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this shape and the spacing of the gas passages being such that a substantially uniform distribution of electric field occurs across the plasma volume space between the electrodes.

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According to the present invention in a second aspect there is provided a reactor wherein the electrodes are embedded in a body of dielectric material which extends across the space between the electrodes and includes a plurality of gas passages extending longitudinally of the body of dielectric material to provide a plurality of electrically equivalent plasma volumes extending in series across the space between the electrodes.

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Preferably the matrix of gas passages in the dielectric medium between the electrodes is adapted to provide a potential difference across the plasma volume space between the electrodes equal to half the supply voltage. The potential difference across this space will vary according to gas flow, temperature and gas composition and therefore the overall size and shape and position of location of the reactor within the exhaust system is selected so as to ensure that variances from this optimum condition are minimized.

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The surfaces of the gas passages can be coated, impregnated or generally treated by for example ion exchange or doping with a material which is catalytically active in relation to the gas and or particulate processing reactions to be carried out in the reactor, or the gas passages can be filled with a gas permeable form of such a material. The geometry of the gas passages or the gas permeable filling material, which may be dielectric, can then be adapted to negate the capacitive effects of the catalytic material. Alternatively, the

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dielectric material of the reactor can itself be chosen to be catalytic in relation to the gas and or particulate processing reactions to be carried out in the reactor. The gas permeable material filling the passages can be

5 catalytically-active or non-catalytically thermally-active with respect to processing of the gaseous medium although a catalytically-active material may be present on the surface of non-catalytic dielectric material contained in the reactor as a coating or it may be

10 present on or in the gas permeable filling material by generally treating the material by for example ion exchange or doping.

Gas permeable dielectric filling material for the

15 reactor can be in the form of spheres, pellets, extrudates, fibres, sheets, wafers, frits, meshes, coils, foams, membrane, ceramic honeycomb monolith or granules or as a coating on any of the above shapes or on a ceramic foam or ceramic honeycomb monolith. In addition

20 to optimising the plasma discharge and gas processing characteristics, combinations of one or more of the above can be used to create a filter structure with a non-uniform surface area and porosity, for example a graded porosity when presented to the exhaust gas particularly

25 when containing particulates as described in patent specification W000/43102. Gas permeable dielectric filling material that can be placed inside the reactor can also be housed outside of the plasma region of the reactor so that the gaseous media can either pass through

30 this material before entering the plasma region or pass through this material after passing through the plasma region. When placed outside the reactor, dielectric filling material can be replaced by ceramic, polymeric or metallic material in the same form described above for

35 the dielectric filling material. Dielectric filling material can act as a selective filter as described in

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C | the specification of our PCT/GB00/3943 ~~respectively~~.  
Dielectric material or trapped species on it in the  
plasma can be made to appear to act as a catalytic  
surface to the gas processing reactions even though  
5 neither the plasma nor the dielectric material nor  
trapped species alone need have catalytic properties as  
described in the specification of our application  
PCT/GB00/3943.

- 10 When the gaseous medium comprises the exhaust gases  
containing nitrogenous oxides and particulate material  
such as carbonaceous particulate that are derived from an  
internal combustion engine supplied with combustion fuel,  
the exhaust gases can contain hydrocarbon either added  
15 separately or residually derived from the fuel  
combustion. The exhaust can contain a chemical additive  
acting as a carbon combustion catalyst that is either  
present initially in the fuel or added separately to the  
exhaust and whose function is to lower the combustion  
20 temperature and/or increase the rate of removal of  
carbonaceous material. Carbon combustion catalyst can be  
encapsulated within or bound to a fugitive additive that  
chemically decomposes during or shortly after fuel  
combustion thus releasing the additive into the fuel or  
25 exhaust. Examples of carbon combustion catalysts are  
alkali-metal salts such as lithium nitrate described in  
GB 2 232 613 B, cerium oxide, alkali-metal doped  
lanthanum oxide-vanadium oxide, perovskites such as  
 $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$  and also layered perovskites or vanadate or  
30 combinations of such materials although such carbon  
combustion catalysts can also constitute all or part of  
the dielectric filling material described above. The  
mode of operation of such catalysts is described in our  
specification WO00/43102. The use of a carbon combustion  
35 catalyst can reduce the power requirements to the plasma

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reactor for treating carbonaceous particulate material and reduce the volume of active material.

For the reduction of nitrogenous material for which  
5 zeolites are particularly useful materials, the plasma  
can produce activated hydrocarbon from hydrocarbon  
reductant in the exhaust as described in our publication  
WO99/12638 and/or convert nitrogenous oxides to nitrogen  
dioxide as described in WO99/12638 and WO00/43102. It  
10 should be appreciated that material that is not catalytic  
for the reduction of nitrogenous material when not  
exposed to a plasma may develop catalytic properties for  
this reduction when exposed to a plasma due for example  
to activation by O atoms or other plasma-generated free  
15 radicals or activation by plasma generated species such  
as activated hydrocarbons and or nitrogen dioxide. It  
should be appreciated that the dielectric filling  
material can also be placed outside the plasma zone and  
outside the reactor with a multiplicity of additive  
20 injection ports as described in WO99/12638. Catalytic  
properties can be further augmented by the electric field  
and or other charged species present in or adjacent to  
the plasma region. A reductant other than hydrocarbon  
may be used, in particular nitrogen containing species  
25 such as ammonia, urea or cyanuric acid. When a nitrogen  
containing species is used as a reductant for  
nitrogenous oxide reduction a particularly useful  
catalyst is vanadium pentoxide-titanium dioxide. When  
using a nitrogen containing reductant species, mixing  
30 with effluent can also be made after the effluent has  
passed through the plasma zone of the reactor before  
contact with the catalyst.

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The invention will now be described, by way of  
35 example, with reference to the accompanying drawings, in  
which



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Figure 1 is a perspective view of the operative part of a reactor embodying the invention for the plasma assisted processing of a gaseous medium, and

- 5        Figure 2 is a transverse section of a second embodiment of the invention.

Referring to Figure 1 of the drawings, the operative part of a reactor for the plasma assisted processing of a  
10        gaseous medium includes two planar electrodes 1 and 2 to one of which is connected a high voltage supply cable 3. The other electrode has a cable 4 connected to it by

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means of which it can be connected to a suitable  
grounding point. The electrodes 1 and 2 are surrounded  
and separated by a body 5 of a dielectric material, which  
supports the electrodes so that there is a substantially  
5 uniform separation of their facing surfaces. The  
dielectric material is required to maintain thermal  
stability across a range of exhaust gas temperatures, and  
is selected from such materials as alpha and gamma  
aluminas, aluminosilicate ceramics, cordierite, silicon  
10 carbide, mullite or a moldable dielectric ceramic  
material such as the micaceous glass MICATHERM as  
disclosed in our patent specification WO99/20373. A  
number of identical gas passages 6 extend through the  
body 5 of dielectric material parallel to the electrodes  
15 1 and 2 and spaced apart from one another in a direction  
transverse to the said facing surfaces so that a uniform  
distribution of electric field occurs across the space  
between the electrodes.

20 The gas passages 6 are separated by regions 7 of  
dielectric medium which are of equal thickness and  
parallel to the electrodes 1 and 2 so as to form a  
distributed dielectric barrier between the electrodes 1  
and 2.

25 The electrical isolation of the gas passages 6 from  
one another prevents the plasma from forming a short  
circuit between the electrodes 1 and 2. Also, it can be  
shown that the maximum coupling of power into the plasma  
30 volume between the electrodes 1 and 2 occurs when the  
potential drop across the plasma volume is equal to half  
the supply voltage. This can be achieved by a suitable  
choice of the number and cross-section of the gas  
channels 6. The supply voltage can be derived from a  
35 resonant power supply that is adjacent thus in close  
proximity to the reactor as described in our publications

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WO99/05400 and the specification of our application  
WO00/43645.

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If desired, the gas channels 6 can be filled with a  
5 gas permeable body made of an insulating material which  
is catalytic or non-catalytic towards the gas and or  
particulate processing reactions to be carried out in the  
reactor. Alternatively, the surfaces of the gas passages  
6 or gas permeable filling material can be coated with  
10 such a catalytic material, or the entire body of  
dielectric can be made of such a material. The choice of  
material, which can by itself be catalytic or non-  
catalytic in the presence or absence of the plasma,  
depends on the requirements to process nitrogeneous  
15 oxides or particulate material and other emissions  
described previously. Dielectric material or trapped  
species on it in the plasma can be made to appear to act  
as a catalytic surface to the gas processing reactions  
even though neither the plasma nor the dielectric  
20 material nor trapped species alone need have catalytic  
properties. Gas permeable dielectric filling material  
that can be placed inside the reactor can also be housed  
outside of the plasma region of the reactor so that the  
gaseous media can either pass through this material  
25 before entering the plasma region or passes through this  
material after passing through the plasma region. It will  
be appreciated that the same material can be used in the  
plasma zone as outside the plasma zone or combinations of  
different materials can be used in the plasma zone and  
30 outside the plasma zone and that exhaust gas and or  
particulate processing reactions can be carried out by  
combinations of identical or different materials in or  
out of the plasma zone.

35 In practice, of course, the operative part of the  
reactor is contained in an envelope which includes inlet

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and outlet stubs by means of which it can be incorporated in pipework through which the gaseous medium to be processed is caused to flow and means for ensuring that all the said gaseous medium passes through the gas passages 6.

Although the invention has been described in terms of a planar geometry as shown in Figure 1, it is equally applicable to a cylindrical geometry as shown in Figure 2, although in this case, the radial thicknesses of the gas passages will have to vary in order that a uniform radial potential drop be achieved. The embodiments of reactor described in these examples may include catalytic components or be installed as part of an emissions control system employing catalysts or other emission control devices for the plasma assisted treatment of the exhaust gases from internal combustion engines. Such other emission control devices may comprise exhaust gas recirculation (EGR), variations in ignition timing, fuel injection timing and fuel injection pulse rate shaping. The reactor of these examples can be used in conjunction with a power supply and engine management system as described in patent specification WO00/50746. An article 'Stop go systems get the green light' in European Automotive Design, April 1998, pages 24-26 describes an example of an integrated starter alternator damper system (ISAD). Such an ISAD can be used as part of a power supply system to power a plasma assisted emissions control system of which a reactor as described herein is part. In addition, other power sources such as but not limited to fuel cells, gas turbines, solar cells and heat exchangers can be the primary or part-provider of the electrical-generating power source that can also be used to power the power supply system for the reactor.

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Referring to Figure 2 a cylindrical reactor body 20 consists of two cylindrical electrodes 21 and 22, which are embedded co-axially in a cylindrical body 23 of a temperature resistant dielectric material. Between the electrodes 21 and 22 are a series of concentric gas passages 24 of cylindrical form separated by radial supporting webs 25. The gas passages 24 are so arranged that they are superimposed radially and each group of gas passages 24 corresponds to the series of gas passages 6 of the Figure 1 embodiment of the invention. (Only two rings of gas passages are shown in the drawing although it will be appreciated that the invention is not restricted to use of only two of such rings).

Unlike the Figure 1 embodiment of the invention, the radial widths of the gas passages 24 are not the same, but are a function of the distance of the centres of the gas passages 24 from the inner electrode 22. This is because the radial distribution of the electric field between the electrodes 21 and 22 also is a function of the radial distance from the surface of the inner electrode 22. By a suitable choice of radial widths for the gas passages 24, these two effects can be made to cancel out, giving substantially equal radial electric fields in each of the gas passages 24.

In this case, the inner electrode 22 is arranged to be the high voltage electrode.

A particular use for such reactors is to reduce the emissions of one or more of nitrogeneous oxides, particulate including carbonaceous particulate, hydrocarbons including polyaromatic hydrocarbons, carbon monoxide and other regulated or unregulated combustion products from the exhausts of internal combustion engines. In this case, suitable dielectric materials for

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the body 5, are alpha and gamma aluminas, cordierite, mullite, alumino silicate ceramics, silicon carbide, micaceous moldable ceramics such as MICATHERM or mixtures of these. Suitable catalytic material that can be used for coating the surfaces of the gas channels 6, or for use as the dielectric filling material or for depositing onto the dielectric filling material, for example as a coating, are aluminas known under their Registered Trade Marks as LD 350, CT 530, Condea hollow extrudates, DYPAC, T-60 Alumina, T-162 alumina cordierite,  $\alpha$ ,  $\chi$  and  $\gamma$  aluminas, and aluminas containing mixtures of these phases, ferroelectric materials such as titanates particularly barium titanate; titania, particularly in the anatase phase; zirconia, vanadia, silver aluminate, perovskites, spinels, metal-doped and metal oxide-doped or exchanged inorganic oxides such as cobalt oxide-doped alumina, vanadates and pyrovanadates and metal-doped zeolites. Examples of zeolites are those known as ZSM-5, Y, beta, mordenite all of which may contain iron, cobalt or copper with or without additional catalyst promoting cations such as cerium and lanthanum. Other examples of zeolites are alkali metal containing zeolites in particular sodium-Y zeolites that are particularly useful for treatment of nitrogeneous oxides. Examples of perovskites are  $\text{La}_2\text{CuO}_4$ ,  $\text{La}_{1.9}\text{K}_{0.1}\text{Cu}_{0.95}\text{V}_{0.05}\text{O}_4$  and  $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ . Examples of vanadates are potassium metavanadate, caesium metavanadate, potassium pyrovanadate and caesium pyrovanadate. Mixtures of these compounds can also be used.

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Gas permeable dielectric filling material for the reactor can be in the form of spheres, pellets, extrudates, fibres, sheets, wafers, frits, meshes, coils, foams, membrane, ceramic honeycomb monolith or granules

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or as a coating on a ceramic foam or ceramic honeycomb monolith. Combinations of one or more of the above can be

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used to create a filter structure with a non-uniform surface area and porosity, for example a graded porosity when presented to the exhaust gas and the filling material can also be placed outside of the plasma region  
5 of the reactor.

Zeolite materials are particularly useful for treatment of nitrogenous oxides while perovskites and vanadates are particularly useful for treatment of  
10 carbonaceous particulates. Perovskites can also be particularly useful for combined removal of nitrogenous oxides and particulate material.

Thus, exhaust gases containing hydrocarbon reductant  
15 residually-derived from the fuel combustion or added separately or containing a nitrogen-containing reductant for reduction of nitrogenous oxides and or containing a carbon combustion catalyst as described earlier is passed through the plasma region of the plasma reactor  
20 containing dielectric material that is catalytically-active for gaseous processing reactions or is passed through such material before entering the plasma region or is passed through such material after passing through the plasma region. When a nitrogen-containing reductant  
25 is used the reductant can be added to exhaust leaving the plasma region of the reactor and before passage over catalytically-active dielectric material.

Also, suitable supply voltages are obtained from a  
30 power supply adapted to produce pulses having a potential of the order of kilovolts to tens of kilovolts and repetition frequencies in the range 50 to 5000 Hz, although higher frequencies of the order of tens of kilohertz can be used. Pulsed direct current is  
35 convenient for automotive use, but alternating potentials

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for example triangular or sine waves of the same or similar characteristics can be used.

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